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High-temperature oxidation behavior of hot-dipped aluminide mild steel with various silicon contents

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ABSTRACT

Mild steel was coated by hot-dipping into molten baths containing pure aluminum, Al–2.5Si, Al–5Si and Al–10Si (wt.%) at 700 °C for 180 s. Isothermal and cyclic oxidations were carried out at 750 °C in static air to study the oxidation behavior of the hot-dipped aluminide steel with various silicon contents. The results of isothermal oxidation show the weight gains of the aluminide steel followed a parabolic law. The isothermal oxidation rates of the aluminide steel specimens were directly proportional to the silicon content in the aluminide layers. The reason for the aluminide steel with high silicon possessing a high isothermal oxidation rate is that the silicon addition in the molten bath caused a reduction in the aluminide layer thickness and the formation of phase transformation induced voids in the aluminide layer. The results, after cyclic oxidation, show the weight gains of the aluminide steel specimens were larger than those after isothermal oxidation. Because the aluminide layer with low silicon was mainly composed of a thick brittle Fe_2Al_5 phase, thermal stress was easily generated in the aluminide layer and caused the formation of vertical cracks when the aluminide steel underwent cyclic oxidation. Once cracks appeared, the weight gains of the aluminide steel specimens were accelerated. Thus, mild steel after hot-dipping in pure aluminum, which had the thickest Fe_2Al_5 layer, possessed the worst resistance to cyclic oxidation.

1. Introduction

Carbon steel has been widely used as a structural material in engineering applications at room temperature due to its low cost and better mechanical properties than iron [1,2]. In a high-temperature environment, however, carbon steel will be oxidized easily and form a non-protective iron oxide scale with a fast growth rate on the surface of the steel. The formation of the non-protective iron oxide scale also indicates the degradation of the mechanical properties of the steel. Hot-dip aluminizing is a surface treatment that places a high-temperature protective aluminide layer on the surface of carbon steel to improve the oxidation resistance of carbon steel. Hot-dip aluminizing can be classified as hot-dip pure aluminum and hot-dip aluminum–silicon according to the chemical composition of the molten bath for hot-dipping [3].

Studies on the microstructure and phase constitution of hot-dipped aluminide carbon steel have indicated that the aluminide layer formed on carbon steel can be recognized as an outer aluminum topcoat and an inner continuous intermetallic layer [3,4]. The intermetallic layer formed on carbon steel after hot-dipping in pure aluminum possesses an outer minor $FeAl_3$ layer and an inner major Fe_2Al_5 layer [5,6]. The intermetallic layer formed on carbon steel after hot-dipping in aluminum–silicon, on the other hand, has not only $FeAl_3$ and Fe_2Al_5 but also τ_5-Al_7Fe_2Si and τ_1-$(Al,Si)_5Fe_3$ phases, which form above $FeAl_3$ and in Fe_2Al_5, respectively. Additionally, it has been reported that silicon addition in the aluminum bath dramatically decreases the thickness of the intermetallic layer and flattens the intermetallic layer/steel substrate interface [4]. Because a thin intermetallic layer and a flat intermetallic layer/steel substrate interface are the desired microstructures that give the hot-dipped aluminide layer better mechanical properties, silicon has been seen as a common added element in the aluminum bath [3,4,7]. The reduction in thickness of the intermetallic layer when silicon is added into the aluminum bath has been explained by silicon in the aluminum bath retarding the growth rate of Fe_2Al_5 and accelerating the spallation rate of the intermetallic layer into the aluminum bath [8,9]. However, the decreasing trend in thickness of the intermetallic layer will be slowed down when the amount of silicon addition reaches 10 wt.%. This is also the reason that the maximum amount of silicon addition in the aluminum bath is 10 wt.% [10].

When hot-dipped aluminide steel is used in an isothermal high-temperature environment, the interdiffusion between the aluminide layer and the steel substrate starts. This causes decrease of aluminum concentration and void formation in the aluminide

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layer [11–13]. On the other hand, the mismatch of coefficient of thermal expansion (CTE) between the aluminide layer and steel substrate leads to crack formation in the aluminide layer when hot-dipped aluminide steel is used in a thermal shock environment [14,15]. The voids and cracks formed in the aluminide layer can be seen as the paths for oxygen in the atmosphere to penetrate inward to the steel substrate through the aluminide layer. Once the iron is oxidized and has formed iron oxide, the steel substrate is no longer protected by the aluminide layer. Many studies [16,17] indicate that silicon addition in the aluminum bath changes the behaviors of microstructure evolution and phase transformation in the aluminide layer after high-temperature exposure. Thus, one can predict that the oxidation resistance of aluminide steel will be influenced by silicon addition in the aluminum bath. Studies concerning the oxidation behavior of hot-dipped aluminide steel [18–20] have revealed that the steel, after hot-dipping in pure aluminum, possesses better isothermal oxidation resistance than steel after hot-dipping in aluminum with 10 wt.% silicon. The reason for this can be attributed to the formation of a large amount of connected voids in the silicon-modified aluminide layer, which increases the possibility of the steel substrate being oxidized. Unfortunately, the investigations focusing on the oxidation behavior of steel hot-dipped in aluminum baths containing different amounts of silicon are limited. In this study, isothermal and cyclic oxidations were performed on mild steel hot-dipped in aluminum baths with different silicon additions at 750 °C. This temperature is the upper limit of the operating temperature for the advanced ultra-supercritical power plant that may be experienced by exposed steel components in the oxidation environment. The oxidation kinetics and microstructures of aluminide steel after oxidation have been examined in order to understand the effect of silicon addition in the aluminum bath on the oxidation behavior of hot-dipped aluminide mild steel.

2. Experimental

2.1. Hot-dip aluminizing

A commercial AISI 1005 steel was used as the substrate material in this study. The chemical composition of the adopted steel is Fe–0.05C–0.24Mn–0.01P–0.01S (wt.%). The surfaces of the steel specimens for aluminizing were finished by grinding with a #1200 SiC paper. During the aluminizing process, the steel specimens were immersed in the pure aluminum, Al–2.5Si, Al–5Si and Al–10Si (wt.%) molten baths at 700 °C for 180 s and then cooled down to room temperature in static air (hereafter termed HDA, HDA2.5S, HDA5S and HDA10S, respectively). Details of the hot-dip aluminizing of steel specimens have been described in our previous study [21].

2.2. High-temperature oxidation

Isothermal and cyclic oxidations were both performed to study the oxidation behavior of the hot-dipped aluminide steel. Each aluminide steel specimen for isothermal and cyclic oxidations was put in a non-reactive alumina crucible and weighed. The crucibles with specimens were then placed in electric resistance furnaces. Isothermal oxidation was conducted at 750 °C in static air for 24–768 h. After isothermal oxidation, crucibles with specimens were cooled down to room temperature in air. The weight changes of specimens after isothermal oxidation were measured together with crucibles by electronic balance (0.1 mg accuracy), and the value of weight change per unit area was averaged from four specimens under each experimental condition. Cyclic oxidation was conducted at 750 °C in static air for 20–720 cycles. Each cycle consisted of 20 min at 750 °C and 60 min at room temperature, which was long enough to cool the crucibles with specimens below 30 °C. The weight changes of specimens after cyclic oxidation were also measured together with crucibles by electronic balance (0.1 mg accuracy).

2.3. Analysis method

Aluminide steel specimens after isothermal and cyclic oxidations were prepared for cross-sectional metallographic examination using standard grinding and polishing. Cross-sectional specimens were observed using field emission gun–scanning electron microscopy (FEG-SEM) in backscattered electron (BSE) mode. This revealed the atomic number contrast images and distinguished phases by their chemical composition differences. The chemical composition analysis of the phases observed from SEM/BSE micrographs was performed by energy dispersive spectroscopy (EDS) used in tandem with the FEG-SEM. Aluminide steel specimens after oxidation were also observed from top-view using FEG-SEM in secondary electron (SE) mode to reveal the surface morphologies of the aluminide layers. The crystallographic structures of the phases presented in the aluminide layers were analyzed by X-ray diffraction (XRD) using monochromatic Cu-Kα radiation at 40 kV and 100 mA.

3. Results and discussion

3.1. Mild steel after hot-dip aluminizing

Cross-sectional micrographs of mild steel hot-dipped in aluminum baths with various silicon additions are shown in Fig. 1. The aluminide layers can be distinguished into an outer aluminum or aluminum–silicon topcoat and an inner continuous intermetallic layer. Meanwhile, several scattered intermetallic phases can be found in the aluminum or aluminum–silicon topcoats. The effect of silicon on the microstructures of the aluminide layers was observed. As the amount of silicon increased, the thicknesses of the intermetallic layers decreased from 130 μm on HDA to 5 μm on HDA10S. Concerning the morphologies of the interfaces between aluminide layers and steel substrates, the rough (serrated-like) morphology in HDA disappeared and turned into a flat morphology as the silicon addition increased to 2.5 wt.%. In our previous studies [8,9], the formation of the intermetallic phase in the aluminide layers on mild steel hot-dipped in aluminum baths with various silicon additions has been investigated. The investigations show that the intermetallic layer of HDA is composed of an outer minor $FeAl_3$ layer and an inner major Fe_2Al_5 layer. Two Fe–Al–Si phases can be found when the silicon addition exceeds 2.5 wt.%. In the intermetallic layers of HDA2.5S, HDA5S and HDA10S, τ_5-Al_7Fe_2Si forms above $FeAl_3$ while τ_1-$(Al,Si)_5Fe_3$ scatters in Fe_2Al_5. The phase identification performed on the scattered intermetallic phases in the aluminum or aluminum–silicon topcoats reveals a needle-like intermetallic phase in HDA, a polyhedral intermetallic phase in HDA2.5S, HDA5S and HDA10S, and a plate-shaped intermetallic phase in HDA5S and HDA10S. These are $FeAl_3$, τ_5-Al_7Fe_2Si and τ_6-Al_4FeSi, respectively. Additionally, in this work, the thicknesses of the intermetallic layers decreasing with the increase of the silicon content in the aluminum baths are consistent with previous studies [7–10]. The reason for the reduction in the thicknesses of the intermetallic layers is due to silicon retarding the growth rate of Fe_2Al_5 and accelerating the spallation rate of τ_5-Al_7Fe_2Si into the aluminum baths [8,9].

3.2. Isothermal oxidation

Fig. 2 is the oxidation kinetics of mild steel hot-dipped in aluminum baths with various silicon additions after isothermal oxidation. All aluminide steel specimens gained weight, and the